

PATENT SPECIFICATION

(11) 1340025

1340025

NO DRAWINGS

- (21) Application No. 26741/71 (22) Filed 19 April 1971
 (31) Convention Application No. 27996 (32) Filed 13 April 1970 in
 (33) United States of America (US)
 (44) Complete Specification published 5 Dec. 1973
 (51) International Classification C08F 25/00, 1/13
 (52) Index at acceptance
 C3G 1BX 1C2 2B 2C 3A2 3C3 3C4 C



(54) MODIFIED THERMOPLASTIC COMPOSITIONS

(71) We, ROHM AND HAAS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of Independence Mall West, Philadelphia, Pennsylvania 19105, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention concerns a multi-stage sequentially polymerized polymer comprising an elastomeric portion having grafted thereon a rigid thermoplastic portion.

Rigid thermoplastic polymers are known and are useful for their balance of physical properties, economy, availability, and lack of suitable substitutes. A widely used category of these rigid thermoplastics is the acrylic polymers such as poly-(methyl methacrylate), and many copolymers of methyl methacrylate, and the modified versions thereof. These thermoplastic polymers, being rigid, are susceptible to breakage during the manufacture, processing, shipment, and use.

It is known that large quantities of elastomeric materials may be blended with these rigid thermoplastic polymers to provide improved resistance to sharp, high velocity impact. These elastomers are blended in variable quantities, ordinarily at least 5 per cent and generally at least 15 per cent based on the weight, in the case of a moulding composition, to improve impact properties. At the 20 per cent by weight elastomer level, the impact strength of poly-(methyl methacrylate) is substantially improved but 25 to 30 per cent elastomer is required to produce a truly impact resistant material with up to 50 per cent being added in some cases. In other cases, where breakage occurs during removal of moulded parts from a mould, amounts of blended elastomer less than 5 per cent by weight can effect substantial improvement. Amounts of the order 0.5 to 5.0 per cent are often effective for this

latter purpose. Although the inclusion of a discontinuous elastomeric phase has succeeded in providing substantial impact resistance such improvement has been at the expense of the optical properties of the rigid thermoplastics.

It is possible to maintain the colour and/or transparency of the rigid polymeric portion by refractive index matching, control of particle size, and the like, but heretofore, there has been a significant haze level in the initial product. This haze progressively increases upon exposure to water, either by immersion or by exposure to high levels of humidity. The effect upon exposure to water is accelerated by heat. The hazing phenomenon manifests itself as the development of a whiteness, which upon examination is found to occur through the entire body of the material and not merely on the surface, although the effect is ordinarily most pronounced thereat. The whiteness progressively increases with continued exposure to water, e.g. by intermittent or continuous immersion or exposure to the elements, until the material becomes opaque. Continued exposure eventually results in crazing and ultimate failure or the material.

It is theorized that haze occurs when water penetrates the material, because of the presence of polymerization ingredients, such as initiators, modifiers, chain transfer agents, soaps and emulsifiers, and the like. Residual amounts of such materials are inevitable inclusions in a polymer when they are included in the polymerization mix, and the removal of such extraneous matter is severely restricted by both technological and economic considerations.

The effect of the water upon the polymeric materials is readily apparent. The nature of the effect is not conclusively known, however, and several explanations have been offered. It is probable that haze formation is a complex effect, attributable to a number of causes. One possible explanation is that the water that penetrates the polymer is adsorbed or absorbed by the elastomeric portion, changing the

50

55

60

65

70

75

80

85

90

BEST AVAILABLE COPY

- refractive index, and thereby interrupting the careful index matching of the components. It has also been suggested that the water collects at the "interfaces" of the rigid and elastomeric portions, creating microvoids. The microvoids would interrupt the refractive index matching and would also induce stress which would subsequently cause the microvoids to propagate, thus producing the crazing.
- The adverse nature of haze upon the highly impact resistant materials heretofore available makes the preparation of a high impact thermoplastic resin with improved haze characteristics a highly desirable end.
- Copending application No. 26742/71 (Serial No. 1340026) discloses the preparation of film-forming hetero-polymer latex particles by a process involving emulsion polymerization to form a first stage, cross-linked, rubbery copolymer, followed by a second polymerization to form a final stage hard polymer directly on to the first stage polymer.
- In accordance with the present invention, there is provided a multi-stage sequentially produced polymer comprising:
- (A) a first, elastomeric portion polymerized from a monomer mix comprising at least 50 weight per cent of one or more alkyl or aralkyl acrylates, 0.05 to 5.0 weight per cent of one or more cross-linking monomers, 0.05 to 5.0 weight per cent of one or more graft-linking monomers having two or more addition polymerizable unsaturated groups which participate in the polymerization reaction at substantially different rates, adapted to attach the elastomeric phase to the rigid phase defined hereinafter, 0 to 10.0 weight per cent hydrophilic monomer or non-hydrophilic monomer which is converted to hydrophilic mers in the elastomeric portion the balance, if any, of said monomer mix being composed of one or more other copolymerizable ethylenically unsaturated monomers; and
 - (B) a final, rigid thermoplastic portion polymerized, in the presence of said elastomeric portion, from a monomer mix comprising at least 50 weight per cent alkyl methacrylate, wherein said elastomeric portion and said thermoplastic portion have a minimum attachment level as hereinafter defined of 20 per cent.
- Among the particular advantages to be obtained with the preferred products of the present invention can be the provision of rigid thermoplastic compositions which have excellent initial impact resistance, and which retain high levels of impact resistance after working and forming, i.e., mechanical mixing on calendar rolls, in mechanical mixers, extruding into sheet, film, or shaped forms, compression or injection molding, and further retain such high impact resistance in use, even upon exposure to environmental effects such as high temperatures, ultra-violet light, water in the form of high humidity or rain or other aqueous environs, and still other elements generally involved in weathering. Further, the preferred products provided by the present invention include materials which can have predetermined and controlled optical characteristics which are excellent and which are likewise retained upon working, forming, use, and with exposure. Still other properties and characteristics can also be notably improved such as the handling characteristics of components, intermediates, and products; the processing characteristics can also be much improved, including such factors as blending characteristics, die swell, the occurrence of non-laminar flow in moulding processes, with attendant facility in filling moulds and the formation of high quality moulded products. Materials prepared in accordance with the present invention in general, also show excellent resistance to staining by contact with extraneous materials, notably lipstick and similar compositions.
- While the products provided by this invention can benefit to some extent from the foregoing advantages, some types of rigid materials benefit more notably in some than in others. For example, impact modified acrylic-type thermoplastics are much more susceptible to the formation of water haze, and the attendant whitening of clear, colourless articles or materials. Or in the case of coloured or pigmented materials, an undesirable colour change and chalking occurs. Impact modification of rigid acrylic thermoplastics as hereinafter disclosed results in the elimination or substantial reduction of haze problems. Vinyl halide polymers on the other hand, are far more susceptible to staining when modified with the impact modifiers of the prior art; when modified in accordance with the present invention, staining can be substantially eliminated.
- The multi-stage polymers of the invention can be so formulated that they can be used *per se* as impact resistant thermoplastics, suitable as a molding powder or the preparation of films or sheets. The multi-stage polymers can also be blended with additional amounts of a rigid thermoplastic, serving as a modifier of the impact properties. Whether used *per se* or in combination with other materials, impact resistance can be attained with low initial haze and resistance to haze increase upon water exposure.
- The multi-stage polymer material is ordinarily prepared by emulsion polymerization, to form the elastomer portion, from a monomer mix of at least 50 weight per cent alkyl and/or aralkyl acrylate, 0.05 to 5.0 weight per cent of a poly-unsaturated cross-linking monomer, 0.05 to 5.0 weight per cent of a graft-linking comonomer, and 0 to 10.0 weight per cent of a hydrophilic comonomer. Upon completion of the polymerization of the elastomeric portion,

- i.e., substantial exhaustion of the monomers in the initial polymerization mix, the rigid thermoplastic can then be formed by polymerization, probably at the surface of the elastomer phase, in the same emulsion, of a monomer mix comprising at least 50 weight per cent (C_1-C_4)-alkyl methacrylate. The monomers which are polymerized to form the rigid thermoplastic portion of the multi-stage polymer are preferably added in such a fashion that substantially all the rigid portion is formed on or at the surface of the elastomeric phase.
- In preferred formulations of the multi-stage polymer, the monomer mix forming the elastomeric portion, contains 0.1 to 1.0 weight per cent of cross-linking comonomer(s), 0.1 to 1.0 weight per cent of graft-linking comonomer(s), and 0.5 to 5.0 weight per cent of hydrophilic comonomer(s), together with at least 50 weight per cent alkyl and/or aralkyl acrylate.
- The acrylic elastomer portion of the multi-stage polymer can be formed from major proportions of alkyl esters of acrylic acid having alkyl groups of one to fifteen carbon atoms, preferably 1 to 8 and most preferably 2 to 8 carbon atoms. Longer chain alkyl groups may be used. Other acrylic monomers, up to 50 weight per cent, less the other inclusions, can also be used, such as alkyl esters of acrylic acid in which the alkyl group is substituted by a carbocyclic or heterocyclic nucleus containing 5, 6 or 7 carbon atoms, with or without an additional alkyl bridge, and the alkyl portion of the substituted alkyl group contains up to 15 carbon atoms. Substituted acrylates or methacrylates including alkylthioalkyl acrylates such as ethylthioethyl acrylate, and alkoxyalkyl acrylates such as methoxyethyl acrylate can also be used. The monomer mix used to form the elastomeric portion may also, for example, contain up to 40 weight per cent of one or more other addition polymerizable monomers such as styrene, α -methyl styrene, vinyl ethers, amides, and esters, vinyl and vinylidene halides.
- The monomer mix for the acrylic elastomeric portion of the multi-stage polymers includes at least one cross-linker particularly polyfunctional unsaturated monomer(s) capable of cross-linking the elastomer, such as polyethylenically unsaturated monomers like polyfunctional acrylates and methacrylates, and monomers capable of ionic and coordinate cross-linking such as acid groups and organic and inorganic bases and other electron donating groups co-ordinating with suitable electrophilic agents. The cross-linked elastomeric portion of the multi-stage polymers can be described as gelled. The polyethylenically unsaturated monomers include polyacrylic and polymethacrylic esters of polyols such as butylene glycol diacrylate, and dimethacrylate, trimethylolpropane trimethacrylate, di- and trivinyl benzene, vinyl acrylate and methacrylate and other cross-linking monomers.
- Preferred are those elastomeric portions which have a glass temperature less than 25°C. More preferred are those elastomeric portions having a glass temperature less than 10°C., and most preferred are those elastomeric portions having a glass temperature less than -25°C. In all cases, these glass temperatures refer to the elastomeric portion of the multi-stage polymer only and do not include any subsequent polymers attached to the particles of the elastomeric portion.
- The preferred elastomeric portions of the multi-stage polymers of this invention include acrylic polymers comprising 50 to 80 parts by weight C_1-C_4 -alkyl acrylate monomer(s), 0 to 40 parts by weight of other ethylenically unsaturated monomer(s), 0.05 to 5 parts by weight of at least one polyunsaturated cross-linking monomer, 0.05 to 5.0 parts by weight of graft-linking monomer(s), and 0 to 10.0 parts by weight of at least one hydrophilic monomer. Most preferred are those acrylic elastomers comprising units from 50 to 100 parts by weight C_1-C_4 -alkyl acrylate monomer(s), 1 to 20 parts by weight other acrylic monomer(s), 5 to 20 parts by weight other ethylenically unsaturated monomer(s), (preferably those other ethylenically unsaturated units being aromatic such as styrene and substituted styrene), 0.1 to 1.0 parts by weight of at least one polyethylenically unsaturated cross-linking monomer unit, 0.1 to 1.0 parts by weight of a graft-linking monomer and 0.5 to 5.0 parts by weight of at least one hydrophilic monomer.
- The inclusions of the cross-linking monomer, the graft-linking monomer and of the hydrophilic monomer in forming the acrylic elastomer portion lead to the substantial improvements in the properties which can be obtained, including reduction of the initial haze level, in the amount and rate of increase of haze upon exposure to water or to weathering. It is not entirely clear how the improvement is attained, but it has been observed that the effects of each are at least cumulative. The inclusion of each of the noted monomers results in some improvements in the properties of the product, but none alone is able to attain the effectiveness of the combination.
- The graft-linking monomers which are used are similar to the cross-linking monomers hereinbefore described except that, for example, whereas a cross-linker usually has a plurality of addition polymerizable unsaturated groups, each of which participate in the polymerization reaction at about the same rate as one another and as the primary monomers, i.e., the alkyl and/or aralkyl acrylate monomers, the other acrylic monomers, and the other reactive monomers, the graft-linking monomers are compounds having two or more addition polymerizable unsaturated reactive groups which participate in the polymerization reaction at substantially different rates. It is preferred

to include compounds where at least one reactive group polymerizes at about the same rate, or slightly slower than the other monomers, while the remaining reactive group or groups polymerize at a substantially different, i.e., slower, rate. The differential polymerization rates result in a residual level of unsaturation in the elastomeric portion, particularly during the latter stages of polymerization and, consequently, at or near the surface of the elastomer particles. When the rigid thermoplastic portion is subsequently polymerized in the presence of the elastomeric portion the residual unsaturated addition polymerizable reactive groups contributed by the graft-linking monomer participate in the subsequent reaction so that at least a portion of the rigid portion is attached to the surface of the elastomer. The extent of the attachment is hereinafter explained more fully.

The compounds particularly preferred for use as graft-linking monomers are allyl methacrylate and allyl acrylate. Other compounds suitable for use as graft-linking monomers include, by way of example, allyl, methallyl, and crotyl esters of acrylic acid, methacrylic acid, maleic acid (mono- and di-esters); fumaric acid (mono- and di-esters) and itaconic acid (mono- and di-esters); allyl, methallyl and crotyl vinyl ether; allyl methallyl, and crotyl vinyl thioether; N-allyl, methallyl or crotyl maleimide; vinyl ester of 3-butenoic and 4-pentenoic acid; triallyl cyanurate; O-allyl, methallyl or crotyl, O-alkyl, aryl, alkaryl or aralkyl, P-vinyl, allyl, or methallyl phosphonate; triallyl, trimethallyl or tricrotyl phosphate; O-vinyl, O,O-diallyl, dimethallyl or dicrotyl phosphate; cycloalkenyl esters of acrylic acid, methacrylic acid, maleic acid (mono- and di-esters), fumaric acid (mono and di-esters), itaconic acid (mono- and di-esters), such as 2, 3, or 4 cyclohexenyl acrylate, bicyclo (2,2,1) hept-5-ene-2-yl esters of acrylic acid, methacrylic acid, maleic acid (mono- and di-esters), fumaric acid (mono- and di-esters) and itaconic acid (mono- and di-esters); vinyl ethers and vinyl thioethers of cycloalkenols and cycloalkene thiols such as vinyl cyclohex-4-ene-1-yl ether, vinyl ether of bicyclo (2,2,1) hept-5-ene-2-ol; vinyl esters of cycloalkene carboxylic acids such as vinyl cyclohex-3-ene-1-carboxylic acid or vinyl bicyclo (2,2,1) hept-5-ene-2-carboxylate.

Among the effective graft-linking monomers, allyl group containing compounds are preferred, particularly allyl esters of ethylenically unsaturated acids. Most preferred are allyl acrylate, allyl methacrylate, diallyl maleate, diallyl fumarate, diallyl itaconate, allyl acid maleate, allyl acid fumarate, and allyl acid itaconate. Another category of allyl compounds which are highly effective, but not so preferred as the foregoing materials, are the diallyl esters of polycarboxylic acids which do not contain polymerizable unsaturation. Where two or

more allyl groups occur in a single compound, one will tend to polymerize with substantially greater ease than another.

The inclusion of the graft-linking monomer into the elastomeric portion operates in a fashion which is incompletely understood. However, it is known that the inclusion of the graft-linking monomer operates in a fashion different from the inclusion of cross-linking monomer alone. The inclusion of cross-linking agents, such as butylene, diacrylate, divinyl benzene, and the like, effectively cross-link the elastomer but do not provide significant graft-linking. To obtain the benefits of this invention it is necessary to provide graft-linking between the elastomer and rigid phase and to effectively cross-link the elastomer. For example, the use of cross-linker alone provides little benefit in the reduction of haze level in the modified rigid thermoplastic polymers. The inclusion of both graft-linking and cross-linking monomers in the elastomers of this invention can reduce haze level, either initially or upon prolonged exposure. It is hypothesized, that the graft-linking monomers affect the interface between the elastomeric portion and rigid portion of the multi-stage polymer in such fashion that haze formation, possibly attributable to accumulation of water at the interfaces, is effectively eliminated in that no "microvoids" are able to form. This hypothesis remains unproven, however, and should not be considered binding. It has been observed that when the elastomer is polymerized without the graft-linking monomer so that the rigid thermoplastic portion is not attached to the elastomer particles as a last stage of the polymerization, or when no rigid phase is polymerized onto the elastomer, i.e., the elastomer and the rigid material are separately prepared and are later combined, the benefits of the present invention cannot be realized.

The mode of operation of the hydrophilic monomer, included in amounts ranging from 0 to 10.0 parts per hundred parts of elastomer, is believed to be understood, but again the evidence is not so conclusive that it should be considered binding. It appears that the hydrophilic monomer serves, when polymerized in the elastomer, to bind whatever amounts of water are transmitted into the composition, in the manner of water of hydration, for example. Any monomer which can be polymerized in the elastomer mix and which is hydrophilic enough to effectively bind water can be used. Among the hydrophilic monomers which can be mentioned, by way of example only, are acrylonitrile, methacrylonitrile, hydroxy-substituted alkyl and aryl acrylates and methacrylates, amino-substituted alkyl and aryl acrylates and methacrylates, polyether acrylates and methacrylates, alkylphosphato-alkyl acrylates and methacrylate, alkyl-phosphono-alkyl acrylates and methacrylates, acrylic acid, methacrylic acid, maleic acid, maleic anhydride, N-

- vinyl pyrrolidone, alkyl and substituted alkyl amides of acrylic acid, methacrylic acid, maleic acid (mono- and di-amides) fumaric acid (mono- and di-amides) itaconic acid (mono- and di-amides), acrylamide, and methacrylamide. Hydrophilic mers in the elastomeric phase may also be incorporated by using non-hydrophilic monomer in the polymerization mix, such monomer being converted at some stage to hydrophilic mers, e.g. by hydrolysis.
- Among the effective hydrophilic monomers, it is preferred to utilize methacrylic compounds, particularly the amides and hydroxy alkyl esters of methacrylic acid; amides and hydroxy alkyl esters of other acids are also preferred, but less so than the corresponding methacrylates which are more readily polymerized.
- While in its broadest terms, the elastomeric phase comprises a polymer of the alkyl acrylate, the cross-linking monomer, the graft-linking monomer, optionally the hydrophilic monomer, and a balance, optionally also, of other acrylic monomers and other non-acrylic monomers, it is possible to point to narrower ranges of components and proportions thereof which have been found to be particularly effective and/or convenient, either in preparation, handling, formulation, or use, and are accordingly preferred. For example, the formulations comprise elastomer portions polymerized from 50 to 99.9 weight percent C_1-C_8 -alkyl acrylate(s), 0 to 49.9 weight per cent other acrylic monomer(s), 0 to 40 weight per cent other ethylenically unsaturated monomer(s), 0.05 to 5.0 weight per cent cross-linking monomer(s), 0.05 to 5.0 weight per cent graft-linking monomer(s), and 0 to 10.0 weight per cent hydrophilic monomer(s). In even more preferred formulations, the elastomer portion will be polymerized from 50 to 80 weight per cent of an alkyl acrylate(s), where the alkyl group contains 2 to 4 carbon atoms more preferably 4 carbon atoms, 0.1 to 10 weight per cent other acrylic monomer(s), 0.1 to 1.0 weight per cent cross-linking monomer(s), 0.1 to 1.0 weight per cent graft-linking monomer(s), 0 to 5.0, more preferably, 0.5 to 5.0, weight per cent hydrophilic monomer(s), and the balance other non-acrylic unsaturated monomer(s), more preferably styrene, α -methyl styrene, and halostyrenes.
- The rigid thermoplastic portion of the multi-stage polymers of this invention include the class known in the art as acrylic polymers. In the invention, these polymers may be characterized as having the majority (viz 50—100%) of alkyl methacrylate units in the polymer. This entire class of acrylic polymers lacks a satisfactory resistance to impact. The rigid acrylic thermoplastic polymers can be durable acrylic polymers containing minor amounts (0 to 40 per cent) of non-acrylic units and mixtures of all acrylic polymers with minor amounts of non-acrylic polymers to provide well-known balances of physical characteristics. Acrylic units are usually alkyl and aryl methacrylates and acrylates. As used in this specification and claims the group alkyl also includes cycloalkyl, bridged and unbridged, while the group aryl also include aralkyl and alkaryl, All these groups may be substituted or unsubstituted. These acrylic polymers have a heat distortion temperature greater than about 20°C, preferably greater than 50°C., for most general purpose applications. The rigid thermoplastic portions of the multi-stage polymers of this invention include copolymers of 50 to 100 per cent alkyl methacrylate, wherein the alkyl group contains 1 to 4, preferably 1, carbon atoms, containing one or more acrylic comonomers in quantities 0 to 50 per cent such as other alkyl and aryl methacrylates, alkyl and aryl acrylates, alkyl and aryl acrylamides, substituted alkyl and aryl methacrylates and acrylates such as halogen, alkoxy, alkylthio, cyanoalkyl, amino, alkylthiol esters, and other substitutions, and 0 to 40 per cent of other unsaturated monomers including acrylonitrile and methacrylonitrile, styrene monomers and substituted styrene monomers, vinyl esters, vinyl ethers, vinyl amides, vinyl ketones, vinyl halides, vinylidene halides, and olefins. Generally, as the comonomer system chosen is softer, less is used in order to retain the rigid characteristic desired.
- Typical of the monomers which may be used to prepare rigid acrylic polymers include esters of acrylic and methacrylic acid such as methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, 2-ethylhexyl, stearyl, cyclohexyl, isobornyl, bornyl, fenchyl, norbornyl, adamantyl, benzyl, and phenyl. Preferred are those alkyl esters of methacrylic and acrylic acids wherein the alkyl group contains 1 to 4 carbon atoms.
- The preferred cycloalkyl esters of methacrylic and acrylic acids have cycloalkyl group containing 4 to 14 carbon atoms. The substituted esters of methacrylic acid and acrylic acid include chlorine and bromine substituted lower alkyl esters; alkoxy substituted lower alkyl esters such as ethoxy and methoxy; alkylthio substituted lower alkyl ester such as ethylthio and methylthio; and cyanoalkyl substituted lower alkyl esters such as cyanoethyl. Styrene monomers include halostyrenes, vinyl toluene, t-butyl styrene, and α -methyl styrene. Vinyl halides and vinylidene halides wherein the halides include chloride, bromide, and fluoride; olefins include ethylene, propylene, isobutylene and the like, can also be utilized.
- The multi-stage acrylic polymers of the present invention are conveniently prepared by suspension or emulsion polymerization procedures utilizing a sequential technique. In simplest form the elastomeric portion is formed in a first stage and the rigid thermoplastic portion is formed in a second stage. Either the elastomeric or

- rigid portions can themselves also be sequentially polymerized. The monomers of the initial stage, together with the initiators, soap or emulsifier, polymerization modifiers and chain transfer agents can be formed into the initial polymerization mix and polymerized, e.g. by heating and mixing the emulsion, in well-known and wholly conventional fashion until the monomers are substantially depleted.
- Monomers of the second, and, in turn, of each additional, if any, stage can then be added with appropriate other materials, e.g., initiator, soap or emulsifier, so that the desired polymerization of each stage occurs in sequence to substantial exhaustion of the monomers. In each stage subsequent to the first, the amounts of initiator and soap, if any, are preferably maintained at a level such that polymerization occurs at the surface of existing particles, and no substantial number of new particles, or "seeds" form in the emulsion. When the elastomeric portion of the multi-stage polymer is itself formed by sequential polymerization, it is preferred to include the graft-linking monomer and the hydrophilic monomer, if any, in the last stage, or last few stages, of the elastomer. Alternatively, these monomers can be present throughout the entire polymerization of the elastomeric portion. The stages can vary in hardness, from a very soft elastomer first stage seed to the hardest rigid thermoplastic. Both the elastomer and the rigid thermoplastic portions can be formed using chain transfer agents.
- Polymerization can be conducted in accordance with known techniques for effecting emulsion or suspension polymerization, with the use of conventional materials, including, for example, free-radical initiators, soaps and emulsifiers, and modifiers of numerous types. Many of such materials are utilized commonly in the form of metal salts, particularly alkali metal salts. It has been noted that the utilization of potassium salts to the exclusion of sodium from the polymerization system provides certain advantages in many cases. Particularly in the cases where the rigid portion of the final product is to any significant extent acrylic, water exposure presents a reduced level of haze when the potassium salts are utilized. It appears that potassium salts are more completely removed if the resulting polymers are water washed, and the minor amounts which remain do not contribute the same effect as in the case of sodium.
- The polymerization reactions can be initiated by either thermal or redox-type initiator systems. Examples of thermal initiators include the organo peroxides, such as benzoyl peroxide, substituted benzoyl peroxides, acetyl peroxides, lauroyl peroxide, t-butyl hydroperoxide, di-t-butyl hydroperoxide; peresters, such as t-butyl peroxy-pivulate; azo-type initiators, such as azo-bis-isobutyronitrile; persulfates, such as sodium, potassium, or ammonium persulfate;
- and peroxyphosphates, such as sodium, potassium, or ammonium peroxyphosphate. Redox initiators include, for example, a combination of a hydroperoxide, such as hydrogen peroxide, t-butyl hydroperoxide, cumene hydroperoxide, or diisopyropyl-benzene hydroperoxide, and a reducing agent such as sodium, potassium or ammonium bisulfite, metabisulfite, or hydrosulfite, sulfur dioxide, hydrazine, ferrous salts, isoascorbic acid, or sodium formaldehyde sulfoxalate.
- Examples of emulsifiers or soaps suited to the polymerization processes which can be used include alkali metal and ammonium salts of alkyl, aryl, alkaryl, and aralkyl sulfonates, sulfates, and polyether sulfates, ethoxylated fatty acids, esters, alcohols, amines, amides, alkyl phenols, complex organo-phosphoric acids and their alkali metal and ammonium salts.
- Chain transfer agents, including mercaptans, polymercaptans, and polyhalogen compounds are often desirable in the polymerization mix.
- Because of the degree of cross-linking in the elastomeric portion and the participation of residual unsaturation of the elastomer portion in the polymerization of the rigid portion, no adequate or meaningful determination of molecular weight can be ascertained. A portion of the rigid phase is chemically bound to the elastomer; an additional portion usually is not. Extraction of the multi-stage polymer permits determination that the unattached portion of the rigid portion has a measurable molecular weight, which varies with the amount of rigid phase and the nature of the polymerization procedure, and which can ordinarily vary from about 50,000 up to as much as 500,000 or even more. The elastomer portion has been ascertained to generally have a swelling ratio (weight of wet, acetone polymer extracted, insoluble polymer/weight of dry, acetone-extracted polymer) ranging from about 2 to 12, while the unextractable portion of the multi-stage polymer as a whole has a swelling ratio the order of about 6 to 16.
- The relative proportions of the elastomeric and thermoplastic portions can vary quite widely. For example, when the multi-stage polymer is intended for recovery from the polymerization and direct utilization, as, for example, a moulding powder it is, of course, necessary to include in the rigid portion polymerization stage or stages sufficient monomer to provide the total contemplated proportion of the rigid thermoplastic. In such cases, the elastomer portion will comprise only a minor amount of the final multi-stage polymer, e.g. as little as 0.5 weight per cent when only minor improvements in impact properties are required or desired. More often, however, larger proportions, e.g. up to 84% by weight, of the elastomeric portion are contemplated, particularly when the multi-stage polymer is intended to be an impact modifying additive to another material (i.e. rigid acrylic thermoplastic of the

same character as the rigid portion of the multi-stage polymer). In such cases, much less rigid portion need be polymerized in the presence of the elastomeric portion. Although 5 as little as 16 weight per cent of the rigid portion can be sufficient, it is ordinarily preferred that the rigid portion be more than 20 weight per cent, more preferably in excess of 25 weight per cent, and for some purposes may 10 even constitute as much as 99.5% by weight of the total multi-stage polymer.

A preferred multi-stage sequentially polymerised polymer comprises: (A) 50 to 80 weight per cent of a first, elastomeric portion polymerised from a first monomer emulsion comprising 50 to 94.3 weight per cent n-butyl acrylate, 5 to 20 weight per cent styrene, 0.1 to 1.0 weight per cent butylene diacrylate, 0.1 to 1.0 weight per cent allyl methacrylate, and 20 0.5 to 5.0 weight per cent of a hydrophilic monomer which is from one or more of an addition polymerisable amide or hydroxylalkyl ester of methacrylic acid, and (B) 20 to 25 weight per cent of a final, rigid thermoplastic portion, polymerised in the presence of said elastomeric portion from a monomer emulsion comprising 90 to 98 weight per cent methyl methacrylate and 10 to 2 weight per cent ethyl acrylate, wherein said elastomeric portion 30 and said rigid thermoplastic portion have a minimum attachment level (as hereinbefore defined) of 20 per cent.

The degree of attachment between the elastomer portion and the rigid portion depends upon a number of factors, primarily the degree of residual unsaturation from the graft-linking monomer units in the elastomer portion when polymerization of the rigid portion commences. The important consideration in the degree of 35 attachment between the phases is not the percentage of the total rigid portion which is attached to the elastomer. Rather, the relative proportions of attached rigid portion to the elastomer portion is significant. The amount 40 of attached rigid portion material is herein considered to be the total rigid portion material in the multi-stage polymer less the amount of extractable rigid portion material. The amount 45 of extractable rigid portion material is determined by repeatedly extracting 0.5 g. of the multi-stage polymer with 20 ml. increments of acetone, recovery of the acetone insolubles, and determination of the weight change. The 50 attachment level referred to later and in the claims, is defined as

Amount of rigid portion attached

Amount of elastomeric portion

The minimum attachment level consistent with the desired objectives has been found to be at least 20%. At attachment levels below about 60 20%, the advantages which can be provided by the present invention diminish rapidly and

below about 15%, such advantages are substantially lost. No ultimate upper limit of attachment has been found to exist, although at very high levels, such as in excess of about 500%, and particularly above about 1000%, flow properties of the multi-stage polymer, and even of blends of such polymers with other materials, are detrimentally effected. Excessively stiff and viscous materials are difficult to form.

While the phenomena involved are not so clearly understood that the following considerations should be considered binding, it does appear that the monomers used to form the rigid portion penetrate and swell the elastomeric portion particles to some extent and are polymerized in the interior thereof. Since such effects undesirably interfere with the impact properties, polymerization conditions are preferred which tend to minimize penetration. The more rapid the polymerization of the rigid portion monomers, the less time is available for penetration to occur. Accordingly, relatively large amounts of initiator, relatively high temperatures, and relatively slow additions of the rigid portion monomers are preferred to minimize penetration. Even when such preferred conditions are observed, some penetration will probably still occur, but will not be so large an element in determining the properties of the multi-stage polymer. It is theoretically desirable, as well, to ensure that encapsulation of the elastomeric portion by the rigid portion occurs; whether such an effect is in fact attained by observance of the preferred conditions has not been ascertained, but the conditions are not inconsistent with such a result, at least where relatively large proportions of the rigid portion are employed.

By control of the polymerization variables, it is possible to control the particle size of the elastomeric portion in the fashion well-known to the art. The particle size is not of critical significance to the present invention, and can range from as low as 500Å, or even less, up to as large as 3000Å or more. When particularly high impact properties are desired, it is preferable to utilize relatively large particles. In the manufacture of molded articles or rigid sheets of high impact strength, it is accordingly preferred that the particle size range from 1300 to 2000Å, more preferably 1600 to 2000Å.

For the preparation of transparent compositions, it is important to match the refractive indices of the elastomeric and rigid portions. Control of the refractive index is accomplished by balancing the various proportions of the diverse monomers.

The multi-stage polymer can also be utilized as an additive to other rigid thermoplastics, generally of the same character as the rigid portion of the multi-phase polymer, to form blends which have modified impact properties. In such cases, the multi-stage polymer can

65

70

75

80

85

90

95

100

105

110

115

120

125

show advantages over blending procedures utilized in the prior art by virtue of the superior handling characteristics, processability, and dispersability properties imparted by the rigid phase of the multi-stage polymer. Severe difficulties arise when an elastomer additive is blended with a rigid thermoplastic because of the tack and cohesiveness of the elastomeric materials heretofore utilized. The multi-stage polymer of the present invention is not tacky and the particles do not coalesce at ordinary handling conditions. Generally the blends are thermoformable compositions containing up to 99% by weight of rigid thermoplastic and more than 1%, by weight of the multi-stage polymer. Thus a particularly preferred blend comprises (A) 10 to 99 weight per cent of a rigid thermoplastic polymer which is one or more of poly (methyl methacrylate) and copolymers of 90 to 99 weight per cent methyl methacrylate and 10 to 1 weight per cent of a multi-stage polymer, wherein the elastomeric portion of said multi-stage polymer is 0.5 to 50 weight per cent of said blend.

Since it is the elastomeric portion of the multi-stage polymer which imparts impact resistance, multi-stage polymer is added to a rigid thermoplastic to form a blend in such proportions that an appropriate proportion of the elastomeric portion is provided and the rigid portion of the multi-stage polymer should be considered as a part of the total rigid material for purposes of determining proportions of such blends.

The amount of elastomeric material in the blends of the multi-stage polymer and a rigid thermoplastic varies greatly depending upon the type of elastomeric material, the type of blended rigid thermoplastic polymer, and the physical characteristics desired in the final product. It is generally desirable to include 0.5 to 50 weight per cent based on the blend of elastomer in a moulding composition to provide significant and commercially important improvements in the processing and physical characteristics. As the elastomer concentration is increased past 50 weight per cent, certain physical characteristics of the blend are adversely affected and the compositions may no longer be considered advantageous. The physical characteristics adversely affected at the high elastomer concentration include modulus, turbidity, hardness, and shrinkage at high service temperatures. Preferably, the elastomer content ranges from 5 to 50 per cent by weight of the blended molding composition, and more preferably is present in the range of 15 to 40 per cent by weight most preferably 25 to 35 weight per cent of the blend.

The blend of the multi-stage polymer and the rigid thermoplastic can be accomplished by any known method. The rigid thermoplastic and multi-stage polymer can be prepared by suspending the multi-stage polymer in the monomer mix used to pre-

pare the rigid thermoplastic or in a monomer-polymer syrup mix which together will yield the desired rigid acrylic thermoplastic polymer. The multi-stage polymer can be placed in the casting mix in the form of an emulsion, suspension, or dispersion in water or an organic compound. The water or organic compound can be removed before or after casting into the rigid thermoplastic. The multi-stage polymer/rigid thermoplastic blend can be milled to form a well dispersed mixture in an extruder, a roll mill or like equipment to prepare a molding composition. The multi-stage polymer and the rigid thermoplastic can be blended together while both are in emulsion, suspension or solution in aqueous or non-aqueous system, the particles being isolated from the water or organic compound by coagulation, spray drying or known means of isolation, and are further processed with or without an intermediate drying step. Another convenient method of blending the multi-stage polymer and the rigid thermoplastic is by suspending the relatively dry coagulated or spray dried multi-stage polymer in the unpolymerized monomer mix for the rigid thermoplastic and then polymerizing the monomer to form the rigid thermoplastic with the multi-stage polymer intermixed therein. The blend of the polymers is then granulated and processed in an extruder, mill, or injection molding equipment. The blended compositions of this invention can also be prepared by merely mixing suspensions of the rigid thermoplastic polymer with a latex of the multi-stage polymer. Alternatively the blend can be made by preparing the multi-stage polymer in suspension, monomer system used to prepare the rigid thermoplastic polymer being then added directly to the suspension of the composite and polymerized and additional emulsifiers or suspending agents being, if necessary, added to generate new particles. Thus the multi-stage polymer and the rigid thermoplastic polymer can be prepared in the same medium and can be washed, isolated and processed directly as a one pot moulding composition.

When the multi-stage polymer is blended with a separate rigid thermoplastic, the materials where the greatest benefits are derived include the rigid acrylic thermoplastics and the rigid vinyl halide thermoplastics.

The rigid thermoplastic suited for blending with the composite interpolymer of this invention include the class commonly known in the art as rigid acrylic polymers, these preferably having 50-100% of methyl methacrylate mers in the polymer. This entire class of rigid acrylic polymers lacks a satisfactory resistance to impact. The acrylic thermoplastic polymers as a class are generally durable acrylic polymers optionally containing minor amounts (up to 10 per cent) of non-acrylic mers and mixtures of all acrylic polymers with minor amounts of non-acrylic polymers to provide

well-known balances of physical characteristics. Acrylic units mers imparting rigidity are those of alkyl and aryl methacrylates and acrylates. As used in this specification, in connection with the rigid thermoplastics to be blended, the group alkyl also includes cycloalkyl, bridged and unbridged, while the group aryl also include aralkyl and alkaryl. All these groups may be substituted or unsubstituted. The acrylic polymers for blending have a heat distortion temperature greater than about 20°C., preferably greater than 50°C., for most general purpose applications. The rigid thermoplastic used for blending include copolymers of 50 to 100 per cent alkyl, preferably methyl, methacrylate containing one or more comonomers in quantities 0 to 50 weight per cent such as other alkyl and aryl methacrylates, alkyl and aryl acrylates, alkyl and aryl acrylamides, substituted alkyl and aryl methacrylates and acrylates such as halogen, alkoxy, alkylthio, cyanoalkyl, amino, alkylthiol esters, and other substitutions, and 0 to 10 per cent of other unsaturated monomer(s) including acrylonitrile and methacrylonitrile, styrene monomers and substituted styrene monomers, vinyl esters, vinyl ethers, vinyl amides, vinyl ketones, vinyl halides, vinylidene halides, and olefins. Generally, as the comonomer system chosen is softer, less is used in order to retain the rigid characteristics desired.

Typical thermoformable compositions may, for example, comprise a blend of more than 1% by weight of multi-stage polymer and up to 99% by weight of a rigid thermoplastic polymer which may be poly(methylmethacrylate), (or a copolymer polymerised from monomers comprising at least 50% by weight of methyl methacrylate), or a poly(vinyl halide), (or, a copolymer polymerised from monomers which preferably comprise at least 80% by weight of vinyl halide).

Polyvinyl halide rigid thermoplastics to be blended include, for example, polyvinyl chloride, copolymers of vinyl chloride, polyvinyl chloride polymers with modifying compounds, halogenated polyvinyl chloride, and plasticized vinyl chloride compositions. It is preferred that the copolymers comprise at least 80% by weight of vinyl halide. The inclusion of the multi-stage polymer in polyvinyl halide compositions can yield many advantages including greatly increased and non-laminar flow at melt temperatures, that is, processing and extruding temperatures and reduced die swell, without significantly affecting the physical characteristics at normal service temperatures, improved impact strength or tensile properties in rigid extruded polyvinyl chloride sheet compositions, improved mechanical properties in plasticized vinyl compositions, excellent die swell properties on extrusion and good weathering properties. The molecular weight and molecular weight distribution of the multi-stage polymers in the PVC compositions is not

critical to the aims, purposes and results of using this invention. For general applications PVC with Fikentscher K-values (for Fikentscher K-values, see Cellulosechemie Vol 13, p.160, 1932) in the range of 40 to 95' are generally used. The Kikentscher K-value is determined by the formula

$$\frac{\text{Log } \eta_{\text{rel}}}{C} = \frac{75 \times 10^{-6} K^2}{1 + 1.5 \times 10^{-3} KC} + 10^{-4} K$$

where C is a constant concentration of polymer in solvent amounting to 0.5 gm/100 ml. η_{rel} is relative viscosity in cyclohexanone at 25°C. and

K is Fikentscher Value.

Irrespective of whether the multi-stage polymer of the present invention is utilized *per se* or as an additive to a rigid thermoplastic, it can be formed, by appropriate techniques, into excellent quality, exceptionally highly impact resistant finished products having low initial haze levels and with reduced susceptibility to weathering phenomena, and particularly to haze level increase upon prolonged exposure to water. The materials provided in accordance with the present invention can form high quality free films, rigid sheet, and molded or extruded articles. Particular areas where the combination of advantageous features obtainable from the materials of the invention, are those where the environment of use requires both impact resistance and good weathering properties, and where water exposure is an incident of use. Examples of such are virtually all outdoor applications, such as lighting fixtures, signs and displays, and the like.

The multi-stage polymers and blends may include, as is common practice, compounds and materials which stabilize the products and inhibit oxidative, thermal, and ultra-violet light degradation. Stabilizers can be included at any stage from the polymerization process whereby the multi-stage polymer and/or the materials with which such polymer is blended are formed, to the step of forming the final product. It is preferred that stabilizers be included early in the life of the product to preclude later degradation. Accordingly, the preferred practice is to include stabilizers in the polymerization process, if compatible therewith, or in the polymer latex resulting from polymerization step.

The oxidative and thermal stabilizers useful in the materials of the present invention include those used in addition polymers generally. They include, for example, hindered phenols, hydroquinones, phosphites, and varieties of substituted members of those groups and mixtures thereof.

The ultra violet light stabilizers can also be those used in addition polymers generally. Examples of ultra violet light stabilizers include various substituted resorcinols, salicyl-

ates, benzotriazoles and benzophenones.

Other inclusions in the materials of the present invention include lubricants, such as stearic acid, stearic alcohol, eicosanol, and other known types; colorants, including organic dyes, such as anthraquinone Red, organic pigments and lakes, such as phthalocyanine Blue and inorganic pigments, such as titanium dioxide and carmine sulfide; fillers and particulate extenders, such as carbon black, amorphous silica, asbestos, glass fibers and magnesium carbonate; plasticizers, such as dioctyl phthalate, dibenzyl phthalate, butyl benzyl phthalate and hydrocarbon oils.

The present invention is exemplified below, some material being included for comparison purposes and parts and percentages being by weight unless otherwise specifically noted:

Example I.

A series of elastomers are prepared to illustrate the effect of the present invention in producing haze resistant high impact rigid thermoplastics. The compositions are varied to show the effect of (1) the inclusion of a graft-linking monomer in the elastomer polymerization mix and (2) the presence of hydrophilic comonomers.

The elastomer compositions are prepared in this Example in accordance with the following procedure:

The elastomer charge used in the formation of the elastomeric portion is emulsified, using an alkali metal salt of dodecylbenzene sulfonic acid as the emulsifier. About 20 per cent of the monomer charge is polymerized with an alkali metal persulfate at elevated temperature to form a "seed". The remainder of the elastomer monomer charge, with the further inclusion of other monomers, as appropriate, is then added and polymerized, substantially to completion, while controlling the soap or emulsifier concentration to prevent the formation of a significant number of new particles. The resultant polymer is retained in dispersion form and an increment of appropriate monomers are polymerized onto the particles to form a subsequent stage of rigid thermoplastic. The multi-stage polymer (representing the sequentially polymerized elastomer and rigid thermoplastic) is isolated from the emulsion by evaporation and dried under reduced pressure. The seed technique affords effective control of the particle size, but, of course, is necessary only to the preparation of relatively large size particles. For small particle sizes, a single stage polymerization of the elastomer can be utilized.

The multi-stage polymer is blended with an appropriate rigid thermoplastic on a roll mill to give a 30 per cent by weight concentration of elastomer in the blend and the latter is compression molded into a slab. The Izod notched impact strength and initial haze are determined, and the slab is then subjected to 100 per

cent relative humidity at 50°C, for an appropriate length of time, when the haze level is again determined.

Six different compositions are prepared and tested in accordance with the above procedure, and the results are reported in Table I. The elastomeric portions in the example all comprise a major amount of butyl acrylate, a minor, but still substantial proportion of styrene, and a minor amount of 1,3-butylene glycol diacrylate. In Table I, these are designed for convenience, respectively, BA, S, and BDA. Other inclusions, and their respective abbreviations appearing in the Table, are allyl methacrylate (ALMA), acrylonitrile (AN), hydroxyethyl acrylate (HEA), methacrylamide (MAM), methyl methacrylate (MMA), and ethyl acrylate (EA). Another matter of convenience in the table is in the representation of the percentages of the components in the multi-stage polymer. The components BA, S, hydrophilic monomer (if any), and MMA total 100 parts by weight, and other inclusions are reported as a percentage by weight based on the foregoing components. In this manner, changes of composition are readily observed. In addition, a convenient shorthand representation of composition and proportions is utilized. All the components of each stage are represented in the heading of the tabulation, separated by a single stroke; components of the elastomeric rigid portions are separated by a double stroke. All the modifier compositions are prepared by the seed technique, and only BA, S, and BDA are included in the initial, seed forming emulsion. Other components of the elastomeric portion are included in the second stage of the polymerization, and conditions are manipulated so that an average particle size of about 1900 Å is attained.

Table I illustrates the beneficial effects of the utilization of a graft-linking monomer and (optionally) a hydrophilic monomer in accordance with the present invention. Run 1, included for comparison and where neither a graft-linking monomer nor a hydrophilic monomer is included in the elastomeric portion, has rather poor haze properties, as is common in the prior art. Run 2 shows the substantial improvement attained when a graft-linking monomer is added to the formulation. Runs 3 and 4 show the contribution of hydrophilic monomer to the composition. The results of combining both features is illustrated in Run 5 and Run 6, and the excellent improvements there show the great improvement attained in the practice of the present invention.

The rigid thermoplastic which is blended with the composite interpolymer varies in molecular weight in some of the runs, but such variation does not preclude direct comparison of the results, since the properties under consideration do not vary substantially within the range of molecular weights employed.

TABLE I

Run	Composition of multi-stage polymer				MMA/EA $\overline{M}_v \times 10^{-3}$ ⁽²⁾	Initial hrs.	24 hrs.	48 hrs.	72 hrs.	120 hrs.	ASTM D-256-56(A)					
	Blended Rigid Thermoplastic						Haze, % ASTM D-1003-61									
	BA/	S/	BDA/	ALMA/ X//			100% RH(3) 50°C.	1/8" Izod Impact (ft.-lb./in. of notch)								
1 57.4	12.6	0.35	—	30	—	96/4	140	10.0	31.6	—	48.6					
2 57.4	12.6	0.35	0.3	—	30	—	96/4	140	4.5	8.7	—					
3 54.6	11.9	0.35	—	3.5AN	30	—	96/4	210	5.9	5.9	8.0					
4 52.5	10.5	0.35	—	7.0AN	30	—	96/4	210	4.9	5.7	8.3					
5 56.4	12.6	0.35	0.3	1.0HEA	30	—	96/4	210	8.2	8.2	9.3					
6 56.7	12.6	0.35	0.14	0.7MAM	30	—	96/4	165	5.0	—	4.5					

(1) X represents a hydrophilic monomer, as designated

(2) \overline{M}_v represents molecular weight as determined by solution viscosity

(3) RH=Relative Humidity

EXAMPLE II.

A series of additional elastomeric portions are prepared to illustrate the use of other hydrophilic monomers, and the advantages which accrue from the inclusion of a hydrophilic monomer, if any, in that portion, of the rigid thermoplastic polymerized onto the elastomer particles. The procedure of Example I is utilized, to provide a multistage polymer hav-

ing an average particle size of about 1900 Å, and the same rigid thermoplastic is utilized for blending in each case. The results are reported in Table II. Notations appearing in Table II are the same as those in Table I, and the following additional materials are included: hydroxyethyl methacrylate (HEMA) and acrylamide (AM).

TABLE II

Run	Composition of multi-stage polymer	MMA/EA $\bar{M}_v \times 10^{-3}$ ⁽²⁾	Haze, % (2)					
			Blended Rigid Thermoplastic			100% RH (3) 50°C.		
			Initial	24 hrs.	48 hrs.	72 hrs.	120 hrs.	1/8" Izod Impact ft.-lb./in. of notch (2)
	BA/S/LDA/ ALMA/X//MMA/X(1)							
1	56.4/12.6/0.35/0.30/1.0 HEA//30/-	96/4	210	8.2	8.3	9.2	10.2	— 1.3
2	57.4/12.6/0.35/0.30/-//30/2.5 HEMA	96/4	210	8.2	8.8	11.0	10.7	— 1.4
3	56.4/12.6/0.35/0.30/1.0 HEMA//30/-	96/4	210	6.9	7.5	8.4	8.4	10.1 1.4
4	56.4/12.6/0.35/0.30/1.0 HEMA//29/1.0 HEMA	96/4	210	3.2	2.9	4.1	—	4.8 1.0
5	56.7/12.6/0.35/0.28/0.70AM//29/1.0 HEMA	96/4	210	6.6	5.1	5.8	—	7.1 1.8

(1) X represents a hydrophilic monomer, as designated
 (2) and (3) See Table I.

EXAMPLE III.
 The following additional runs are made to show the effect of still other hydrophilic monomers. Methacrylamide (MAM), N-isopropyl acrylamide (NIPAM), and hydroxypropyl methacrylate (HPMA) are utilized.

monomers. Methacrylamide (MAM), N-isopropyl acrylamide (NIPAM), and hydroxypropyl methacrylate (HPMA) are utilized.

monomers. Methacrylamide (MAM), N-isopropyl acrylamide (NIPAM), and hydroxypropyl methacrylate (HPMA) are utilized.

TABLE III

Run	Composition of multi-stage polymer	MMA/EA \bar{M}_v $\times 10^{-32}$	Blended Rigid Thermoplastic		Haze, % (2)		1/8" Izod Impact Str. ft.-lb./in. of notch (2)	
			Initial hrs.	24 hrs.	24	48 hrs.	72 hrs.	120 hrs.
BA/S/BDA/ALMA/X//MMA (1)								
1	56.7/12.6/0.35/0.14/0.7 MAM//30	96/4	210	2.9	—	—	3.5	—
2	56.7/12.6/0.35/0.14/0.7 NIPAM//30	96/4	210	2.8	—	—	4.0	—
3	56.4/12.6/0.35/0.14/1.0 HPMA//30	96/4	210	7.3	—	—	8.0	—

(1) X represents a hydrophilic monomer, as designated.
(2) See Table I.

EXAMPLE IV.

A multi-stage polymer is prepared by the procedure of Example I, having the following composition on a weight basis:

5	butyl acrylate	55.7
	styrene	12.8
	butylene glycol diacrylate	0.35
	allyl methacrylate	0.14
10	hydroxypropyl methacrylate	1.0
	ethylthioethyl methacrylate	0.5
	methyl methacrylate	28.5
	methyl acrylate	1.5

second stage. The methyl methacrylate and the methyl acrylate were added after the polymerization of the other monomers was substantially complete to provide subsequently an attached rigid thermoplastic portion. The latex resulting from the polymerization was spray dried to recover the solid particulate composite polymer, having an average particle size of about 1600 Å.

The multi-stage polymer was then blended with three rigid acrylic thermoplastics in amounts sufficient to provide loadings of 20 and 30 weight per cent elastomer (The methyl methacrylate-methyl acrylate stage is not a part of the elastomer, but rather is calculated as a portion of the rigid thermoplastics.) The blends of the rigid thermoplastics and the multi-stage polymer were then extensively tested to ascertain the physical properties. The results of the testing are reported in Table IV, together with the corresponding values for the unmodified rigid thermoplastics. The three

25

30

The sequential polymerization of Example 15 I is conducted so that the "seed" comprised a portion of all the monomers forming the elastomeric portion, including butyl acrylate, styrene, and butylene diacrylate, allyl methacrylate, hydroxypropyl methacrylate, and ethylthioethyl methacrylate. The balance of these were added to the base emulsion in a

40

20

rigid thermoplastics, designated A, B and C in Table IV had the following compositions and properties:

A: 95.6 wt.% methyl methacrylate, 4.4 wt.% ethyl acrylate, transparent, colourless,
 $M_v = 110,000$.

B: 99.0 wt.% methyl methacrylate, 1.0% ethyl acrylate, transparent, colourless,
 $M_v = 110,000$.

C: 96.5 wt.% methyl methacrylate, 3.5 wt.% ethyl acrylate, transparent, colourless,
 $M_v = 155,000$.

In Table IV the abbreviation TWLT refers

to the ASTM designation for total white light transmittance, and tensile elongation at break refers to the microtensile values, ASTM D-228-69, Type L bar at 0.03 inch/minute. The abbreviation VHT Impact refers to the variable height impact tensile values obtained on the tester supplied in commerce by Gardner Laboratories, Bethesda, Maryland, U.S.A. In this test, a steel slug weighing two or four pounds is dropped from varying heights to a dart with a 3/16 inch radius point in contact with the sample. The force, measured in inches-pounds, is reported at which 50% breakage is obtained. The other tests are standard ASTM procedures.

TABLE IV

EXAMPLE V.

A multi-stage polymer in accordance with the present invention is formed as follows:

5 A first stage elastomeric polymer is prepared from an emulsion of the following monomers in the proportions by weight as designated:

	butyl acrylate	55.70
	styrene	12.80
10	butylene glycol diacrylate	0.35
	allyl methacrylate	0.14
	hydroxypropyl methacrylate	1.00
	ethylthioethyl methacrylate	0.50

15 Upon substantial exhaustion of the monomers of the first stage polymerization, a second, rigid stage is prepared by polymerization on the surface of the first stage of the following mono-

mers, in the designated proportions by weight:

methyl methacrylate	28.5
methyl acrylate	1.5

20

The multi-stage polymer latex is added directly to molten rigid thermoplastic A of Table IV, to provide a blend containing 30% elastomeric material, in a starved-screw devolatilizing extruder maintained at an elevated pressure. Water is removed in the liquid phase from the blend. A minor amount of residual water and unpolymerized monomers are vented under reduced pressure in the barrel of the extruder. The blend is extruded and chopped to provide a granular moulding powder, a portion of which is then formed into slabs having the properties designated in Table V.

25

30

TABLE V

	Rigid Thermoplastic	Blend
Izod Impact (ft. lb./in.), 23°C 1/8" milled notch	0.32	1.8
1/8" molded notch	0.22	1.6
Tensile Impact (ft. lb./in. ²), 23°C	31.5	56.0
Tensile Properties % Elongation at Break	3.9	40—50
Max. Stress, psi	9780	4850
Modulus, psi × 10 ⁻³	4.49	2.12
Flexural Properties Max. Stress, psi	11,850	7250
Modulus, psi × 10 ⁻³	4.52	2.27
HDT (264 psi), °C	82	71
Optical Properties TWLT	92.0	90.0
Haze, %	2.5	4.0

35	An additional increment of the molding powder of the present example was extruded and blown to form a 10 mil free film having the following properties:	Brittleness Temperature	-1°C.
		Haze, %	
		Initial	4
		7 Days Water Immersion, 43°C	4
		16 hrs. Recovery, Ambient Cond.	4
40	Tensile Properties Break Strain, %	30	50
	Break Stress, 10 ³ psi	4.8	
	Elastic Modulus, 10 ³ psi	2.4	
	Work to Rupture, 10 ³ in-lb/in ²	1.5	
45	Fold Endurance Cycles to Fail, × 10 ³	0.4	

EXAMPLE VI.

A multi-stage polymer is prepared in accordance with the present invention by the procedure followed in Example V, except that the second, rigid polymer-forming stage is polymerized from sufficient of the monomers

55

	therein specified so that the multi-stage polymer contains 30 per cent elastomeric portion. The resultant latex is fed under pressure to the starved-screw extruder utilized in Example V and the aqueous medium is removed in the liquid phase at elevated pressure. The resultant moulding powder does not differ markedly in properties, when moulded or extruded into a final product, from the product of Example V.	<i>Third Stage</i>	
5		methyl methacrylate	18.0
		styrene	10.5
		methyl acrylate	1.5
10	EXAMPLE VII.		
15	The multi-stage polymer latex of Example V is blended with a molten rigid thermoplastic, utilizing the same procedure as Example V. In the present example, the rigid thermoplastic comprises 62% methyl methacrylate, 20% butyl acrylate, 12% ethyl acrylate, and 6% isobornyl methacrylate, and has a molecular weight of about 165,000. The resultant moulding powder has substantially improved impact characteristics, low initial haze, and low susceptibility to haze increase upon exposure to water.		50
20	EXAMPLE VIII.		
25	A multi-stage polymer in accordance with the present invention is prepared in a three stage procedure wherein the second stage polymer has properties intermediate to and between the characteristics of the first elastomer portion and the final rigid portions. The monomers utilized in the preparation of the composite are, by stages as follows:		55
30			60
35	<i>First Stage</i>		65
	butyl acrylate	31.4	
	styrene	4.5	
	ethylthioethyl methacrylate	0.5	
	butylene glycol diacrylate	0.18	
	allyl methacrylate	0.07	
40	<i>Second Stage</i>		70
	styrene	28.6	
	butyl acrylate	5.0	
	divinylbenzene	0.3	
	allyl methacrylate	0.07	
			75
			80
	The multi-stage polymer is incorporated into a rigid acrylic-styrene thermoplastic copolymer (MMA/S=65/35), having a molecular weight of about 120,000, in an amount sufficient to provide a loading of 15% elastomer, wherein the second and third stages of the composite are considered to be a portion of the rigid thermoplastic material. The result of the blend is then extensively tested to ascertain the physical properties. The results of the testing are recorded in Table VI together with the corresponding values for the unmodified acrylic-styrene rigid thermoplastic.		

TABLE VI

	Rigid Thermoplastic	Blend
Izod Impact (ft. lb./in.), 23°C 1/8" milled notch	0.40	1.0
1/8" molded notch	0.30	0.8
Tensile Impact (ft. lb./in. ²), 23°C	35.0	48.0
Tensile Properties % Elongation at Break	4.5	5.5
Max. Stress, psi	10,000	5,100
Modulus, psi × 10 ⁻⁵	4.6	2.31
Flexural Properties Max. Stress, psi	12,250	7,500
Modulus, psi × 10 ⁻⁵	4.30	2.17
HDT (264 psi), °C	85	78
Optical Properties TWLT, %	90	89
Haze, %	3.0	5.0
After 48 hrs. at 100% R.H. and 50°C, TWLT, %	90.2	87
Haze, %	3.1	6.0
After 72 hrs. recovery RT TWLT, %	90.1	88
Haze, %	2.9	4.5

EXAMPLE IX.

5 A three stage polymer similar to that of Example VIII, and formed in the same polymerization technique but retained in emulsion form upon the completion of the processing, was formed from the following monomer components:

	First Stage	
10	butyl acrylate	35.6
	styrene	4.5
	ethylthioethyl methacrylate	0.5
	butylene glycol diacrylate	0.2
	allyl methacrylate	0.08

	Second Stage	
15	styrene	24.4
	butyl acrylate	5.0
	divinylbenzene	0.3
	allyl methacrylate	0.06

Third Stage	20
methyl methacrylate	21.0
alpha-ethylstyrene	7.5
methyl acrylate	1.5

The multi-stage polymer latex is added directly to a molten rigid plastic polymer of 25 the following monomer components:

First Stage	20
methyl methacrylate	73.0
alpha-methylstyrene	24.0
ethyl acrylate	2.0
ethylthioethyl methacrylate	1.0

30 The latex was added to provide a blend containing 17% elastomeric portion, in a starved-screw devolatilizing extruder maintained at elevated pressure. The water of the system is removed in the liquid phase from the blend. Minor amounts of residual water

and unpolymerized monomers are vented under reduced pressure in the barrel of the extruder. The blend is extruded and chopped to provide a granular moulding powder, a portion of which is then compression moulded into slabs having the properties designated in Table VII which includes the properties of the unmodified, rigid thermoplastic polymer.

TABLE VII

	Rigid Thermoplastic	Blend
Izod Impact (ft. lb./in.), 23°C 1/8" milled notch	0.30	1.0
1/8" molded notch	0.25	0.9
Tensile Impact (ft. lb./in. ²), 23°C	30	45
Tensile Properties % Elongation at break	2.5	4.0
Max. Stress, psi	10,000	5,200
Modulus, psi $\times 10^{-5}$	4.65	2.29
Flexural Properties Max. Stress, psi	12,000	7,400
Modulus, psi $\times 10^{-5}$	5.3	2.25
HDT (264 psi), °C	105	95
Optical Properties TWLT, %	90	88
Haze, %	2.5	4.0
After 48 hrs. at 100% R.H. and 50°C., TWLT, %	90	87
Haze, %	3.0	4.5
After 72 hrs. recovery RT TWLT, %	90	88
Haze, %	2.8	4.5

10 WHAT WE CLAIM IS:—

1. A multi-stage sequentially produced polymer comprising
 (A) a first, elastomeric portion polymerized from a monomer mix comprising at least 50 weight per cent of one or more alkyl or aralkyl acrylates, 0.05 to 5.0 weight per cent of one or more cross-linking monomers, 0.05 to 5.0 weight per cent of one or more graft-linking monomers having two or more addition polymerizable unsaturated groups which participate in the polymerization reaction at substantially different rates, adapted to attach the elastomeric phase to the rigid phase defined hereinafter, 0 to 10.0 weight per cent hydrophilic monomer or non-hydro-

philic monomer which is converted to hydrophilic mers in the elastomeric portion the balance, if any, of said monomer mix being composed of one or more other copolymerizable ethylenically unsaturated monomers; and

15 (B) a final, rigid thermoplastic portion polymerized, in the presence of said elastomeric portion, from a monomer mix comprising at least 50 weight per cent alkyl methacrylate,

20 wherein said elastomeric portion and said thermoplastic portion have a minimum attachment level as hereinbefore defined of 20 per cent.

25 2. A polymer according to Claim 1, wherein said elastomeric portion is present in an

5

30

35

40

- amount of 0.5 to 84 weight per cent and said rigid phase is present in an amount of 99.5 to 16 weight per cent, based on the weight of said polymer.
3. A polymer according to Claim 1, wherein said elastomeric portion is polymerized from a monomer emulsion comprising about 50 to 99.9 weight per cent of at least one C_1-C_6 -alkyl acrylate, 0.05 to 5.0 weight per cent cross-linking monomer, 0.05 to 5.0 weight per cent graft-linking monomer, 0 to 10.0 weight per cent hydrophilic monomer, 0 to 49.9 weight per cent other acrylic monomers, and 0 to 40 weight per cent other non-acrylic ethylenically unsaturated monomers.
4. A polymer according to Claim 3, wherein said alkyl acrylate is butyl acrylate.
5. A polymer according to Claim 3 or 4, wherein said cross-linking monomer is present in an amount of 0.1 to 1.0 weight per cent.
6. A polymer according to any of Claims 3—5, wherein said cross-linking monomer is a polyethylenically unsaturated monomer having a plurality of addition polymerizable reactive groups all of which polymerize at substantially the same rate of reaction.
7. A polymer according to any of Claims 3—6, wherein said cross-linking monomer is one or more of a polyacrylic ester of a polyol, a polymethacrylic acid ester of a polyol, a poly(vinyl-substituted) aromatic compound, vinyl acrylate and vinyl methacrylate.
8. A polymer according to any one of Claims 3—7, wherein said graft-linking monomer is present in an amount of 0.1 to 1.0 weight per cent.
9. A polymer according to any one of Claims 3—8, wherein said graft-linking monomer is a polyethylenically unsaturated monomer having a plurality of addition polymerizable reactive groups, at least one of which polymerizes at a substantially different rate of polymerization from at least one other of said reactive groups.
10. A polymer according to Claim 9, wherein said graft-linking monomer is an allyl ester of an addition polymerizable ethylenically unsaturated carboxylic acid, a polyallyl ester of a polycarboxylic acid or a mixture thereof.
11. A polymer according to Claim 10, wherein said graft-linking monomer is allyl acrylate, allyl methacrylate, diallyl maleate, diallyl fumarate, diallyl itaconate, allyl acid maleate, alkyl acid fumarate, alkyl acid itaconate, or a mixture thereof.
12. A polymer according to any one of Claims 3—11, wherein said hydrophilic monomer is present in an amount of 0.5 to 5.0 weight per cent.
13. A polymer according to any one of Claims 3—11, wherein a hydrophilic monomer is included and is one or more of addition polymerizable amides of ethylenically unsaturated carboxylic acids and hydroxy alkyl esters of ethylenically unsaturated carboxylic acids.
14. A polymer according to Claim 13, wherein said hydrophilic monomer is one or more of addition polymerizable amides of methacrylic acid and hydroxy alkyl esters of methacrylic acid.
15. A polymer according to any one of the preceding claims, wherein said rigid thermoplastic portion is polymerized from a monomer mix comprising 50 to 100 weight percent C_1-C_6 -alkyl methacrylate, 0 to 50 weight per cent other acrylic monomer(s), and 0 to 40 weight per cent of other ethylenically unsaturated monomer(s).
16. A polymer according to Claim 15, wherein said alkyl methacrylate is methyl methacrylate.
17. A polymer according to Claim 15 or 16, wherein said other acrylic monomer(s) is one or more of alkyl acrylates and methacrylates, aryl acrylates and methacrylates, alkyl acrylamide and methacrylamides, and such monomers substituted with halogen, alkoxy, alkylthio, cyano or amino groups.
18. A polymer according to any of Claims 15—17, wherein said other ethylenically unsaturated monomer is one or more of styrene, substituted styrenes, vinyl esters, vinyl ethers, vinyl amides, vinyl ketones, vinyl halides, vinylidene halides, olefins, acrylonitrile and methacrylonitrile.
19. A polymer according to any one of the preceding claims wherein said first, elastomeric portion is polymerized from a monomer mix to the substantial depletion of the monomers and thereafter said final rigid thermoplastic portion is polymerized from a monomer mix, in the presence of said elastomeric portion, to the substantial depletion of said monomers.
20. A polymer according to Claim 19, wherein said monomer mixes are aqueous emulsions.
21. A multi-stage sequentially polymerized polymer comprising:
- (A) 59 to 80 weight per cent of a first, elastomeric portion polymerized from a first monomer emulsion comprising 50 to 94.3 weight per cent n-butyl acrylate, 5 to 20 weight per cent styrene, 0.1 to 1.0 weight per cent butylene diacrylate, 0.1 to 1.0 weight per cent allyl methacrylate, and 0.5 to 5.0 weight per cent of a hydrophilic monomer which is from one or more of an addition polymerizable amide or hydroxyalkyl ester of methacrylic acid, and
- (B) 20 to 50 weight per cent of a final, rigid thermoplastic portion, polymerized in the presence of said elastomeric portion from a monomer emulsion comprising 90 to 98 weight per cent methyl methacrylate and 10 to 2 weight per cent ethyl acrylate, wherein said elastomeric portion and said rigid

thermoplastic portion have a minimum attachment level (as hereinbefore defined) of 20 per cent.

22. A thermoformable composition comprising a blend of up to 99 weight per cent of a rigid thermoplastic polymer and more than 1 weight per cent of a multi-stage polymer according to any of the preceding claims, wherein the elastomeric portion of said multi-stage polymer constitutes 0.5 to 50 weight per cent of said blend.

23. A composition according to Claim 22, wherein said elastomeric portion constitutes 15 to 40 weight per cent of said blend.

24. A composition according to Claim 22 or 23, wherein said rigid thermoplastic blended with the multi-stage polymer is one or more of poly(methyl methacrylate), copolymers polymerized from monomers comprising at least 50 weight per cent methyl methacrylate, poly(vinyl halide), and copolymers polymerized from monomers comprising at least 80 weight per cent vinyl halide.

25. A thermoformable composition comprising a blend of

(A) 10 to 99 weight per cent of a rigid thermoplastic polymer which is one or more of poly(methyl methacrylate) and copolymers of 90 to 99 weight per cent methyl methacrylate and 10 to 1 weight per cent ethyl acrylate, and

(B) 90 to 1 weight per cent of a multi-stage polymer according to Claim 21, wherein the elastomeric portion of said multi-stage polymer is 0.5 to 50 weight per cent of said blend.

26. A composition according to Claim 24, wherein said elastomeric portion constitutes 25 to 35 weight per cent of said blend.

27. A thermoformed product formed from a polymer according to any of Claims 1—21 or a composition according to any of Claims 22—26.

For the Applicants,
P. W. S. WOOD,
c/o Lennig Chemicals Limited,
26—28 Bedford Row,
London, WC1R 4HU.
Chartered Patent Agent.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.